

REMARKS

Applicant has amended claim 2 to emphasize distinguishable features of the claimed cyclic carbonate-containing polymeric compound and method for producing the same. The claim language is supported by the as-filed specification, e.g., page 8, lines 22-23. No new matter has been introduced.

Applicant respectfully traverses the 35 U.S.C. §§ 102(a) or 103(a) rejection of claims 1, 2, and 6-8 over Saito et al., *Preparation of Cyclic Carbonated Natural Rubber via Supercritical Carbon Dioxide Fixation*, abstract, the 6th Discussion Meeting on Elastomers, the Journal of Society of Rubber Industry, Japan, December 2, 2004 ("Saito"). Saito does not qualify as prior art against the claims. The relevant prior art date listed on the face of Saito is December 2, 2004, which is subsequent to Applicant's March 1, 2004 priority date under 35 U.S.C. § 119. Under 37 CFR § 1.55(a)(4)(i)(B), Applicant submits with this Reply to Office Action an accurate English translation of Applicant's foreign priority document, JP 2004-056275, to perfect Applicant's priority date, along with a statement that the translation is accurate, thereby removing Saito as a prior art reference, under 35 U.S.C. § 102(a) and 35 U.S.C. § 103(a).

Applicant respectfully traverses the 35 U.S.C. §§ 102(b) and 103(a) rejection of claim 1 over SU 422262 ("SU '262"). Applicant also respectfully traverses the § 103(a) rejection of claims 1-8 over SU '262 in view of JP 2002-053573 ("JP '573"), and the § 103(a) rejection of claims 1-8 over SU '262 in view of Kawanami et al., *Research of carbonate synthesis using supercritical carbon dioxide and ionic liquid*, Abstracts of Presentation, the 35th Fall Meeting of Society of Chemical Engineers, Japan, September 18-20, 2002, Vol. 35, p. 391 ("Kawanami").

Catalytic Activity of Various Salts in the Reaction of 2,3-Epoxypropyl Phenyl Ether and Carbon Dioxide under Atmospheric Pressure

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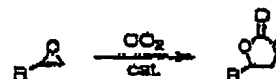
Received January 28, 1993*

Reaction of 2,3-epoxypropyl phenyl ether (1) with carbon dioxide was carried out under atmospheric pressure in *N*-methylpyrrolidinone (NMP) at 100 °C in the presence of 5 mol % of various salts to obtain a five-membered cyclic carbonate, 4-(phenoxymethyl)-1,3-dioxolan-2-one (2), selectively. Only halide salts showed high catalytic activity, and the order of intrinsic activity was found to be as follows: chloride > bromide > iodide which is the order of nucleophilicity of the anion. Furthermore, the order of the activity was found to be lithium salt > sodium salt > benzyltrimethylammonium salt, which is in accord with the order of Lewis acidity of the cation. Kinetic analyses show that the reaction rate can be represented by $-d[1]/dt = k[1][cat.]$, where the carbon dioxide pressure shows no effect on the reaction rate. The reaction proceeds via nucleophilic attack of halide to oxirane to form β -haloalkoxide 4 which reacts with CO₂ followed by cyclization. The presence of key intermediate 4 was indirectly proved by the reaction of 1 with 1 equiv of LiBr in the absence of CO₂ at 100 °C for 2.5 h in NMP which leads to 1-phenoxy-2-propanone (6) in 20 % yield as the rearrangement product of 4.

Recently, the chemistry of carbon dioxide has received much attention,¹ and its reaction with oxiranes leading to five-membered cyclic carbonates (oxirane-CO₂ reaction, Scheme I) is well-known among many examples.² These carbonates can be used as aprotic polar solvents³ and sources for polymer synthesis.⁴⁻¹⁰

Many organic and inorganic compounds including amines,¹¹ phosphines,¹² quaternary ammonium salts,^{2,13} alkali metal salts,^{2,14,15} halostannanes,^{14,15} antimony compounds,¹⁶ and porphyrin^{17,18} and transition-metal complexes¹⁹⁻²¹ are known to catalyze the oxirane-CO₂ reaction. Alkali metal salts have been used not only alone but also in combination with crown ether¹³ or inorganic supports²² because they have been thought to be less active in comparison with lipophilic catalysts.¹² Although many

Scheme I
oxirane-CO₂ reaction



catalysts have been reported, the structure-activity relationship of the catalyst based on a reaction mechanism have not been fully understood.^{12,14,23}

In the oxirane-CO₂ reaction, high pressure of CO₂ has been thought to be necessary.^{2,12} The oxirane-CO₂ reactions under atmospheric pressure have been reported only recently. Reaction of vinyl oxirane with CO₂ under atmospheric pressure in the presence of a palladium complex was reported by Fujinami *et al.*,²⁰ and Takeda *et al.* reported a porphyrin complex-catalyzed oxirane-CO₂ reaction under atmospheric pressure,¹⁷ where the polymerization of oxirane occurs simultaneously. Brindöpke¹¹ reported in a patent a quantitative oxirane-CO₂ reaction under atmospheric pressure in the presence of ammonium salts, amines, or phosphines. He also reported, however, that alkali metal salts can be used as cocatalysts although they were not recommended as main catalysts. On the basis of the report, Rokicki *et al.*²⁴ demonstrated the reaction of an oxirane having an ammonium substituent with CO₂ under atmospheric pressure. Very recently, Nishikubo *et al.* reported that polymer-supported ammonium salts catalyzed the oxirane-CO₂ reaction under atmospheric pressure.²⁵

Recently, we have described the reaction of CO₂ and poly(glycidyl methacrylate) as polymeric oxirane in *N,N*-dimethylformamide (DMF) under atmospheric pressure.²⁶

- * Abstract published in *Advances ACS Abstracts*, October 1, 1993.
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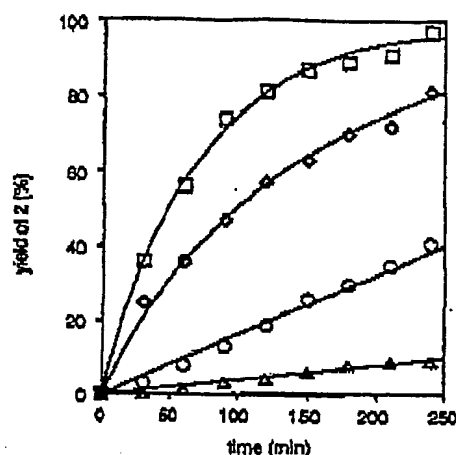
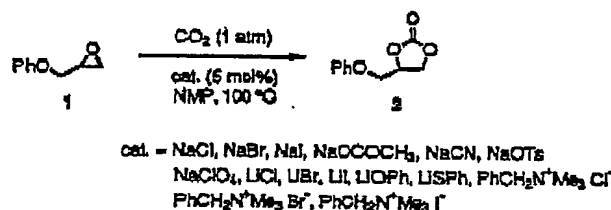
Catalytic Activity in Oxirane-CO₂ Reaction

Figure 1. Yield of 2 vs reaction time for the reaction of 1 with carbon dioxide under atmospheric pressure at 100 °C using NaBr (□), NaI (◊), NaCl (○), and NaOAc (Δ) as catalysts.

Scheme II



Although alkali metal salts had been thought to be not so active catalysts, we found for sodium iodide a higher activity than for triphenylphosphine or benzyltrimethylammonium iodide. We assumed that in homogeneous systems, such as in DMF solution, the intrinsic activity of alkali metal salts may be higher compared with phosphines or ammonium salts. Thus, we undertook detailed studies on the catalytic activity of various salts on the oxirane-CO₂ reaction using 2,3-epoxypropyl phenyl ether as model oxirane in an aprotic dipolar solvent under atmospheric pressure.

In this paper, we wish to report our findings: (1) only halides show high catalytic activity under atmospheric pressure, (2) alkali metal halides are more effective catalysts than onium salts, (3) the pressure of CO₂ does not affect the reaction rate, and (4) establishment of reaction mechanism.

Results

2,3-Epoxypropyl phenyl ether (1) was used as oxirane, and the reaction was carried out in NMP at 100 °C under 1 atm of CO₂ in the presence of 5 mol % of the salts. The conversion of 1 and the yield of a five-membered cyclic carbonate, 4-(phenoxyethyl)-1,3-dioxolane-2-one (2), were monitored by HPLC (Scheme II).

First of all, the reaction of 1 and CO₂ was carried out using sodium salts, including iodide, bromide, acetate, cyanide, *p*-toluenesulfonate, and perchlorate, as catalysts. In these cases, the yield of 2 corresponded to the conversion of 1, and no byproduct could be detected by HPLC analysis. Typical time-yield curves are shown in Figure 1. To describe the activity of the catalyst, eq 1 was assumed:

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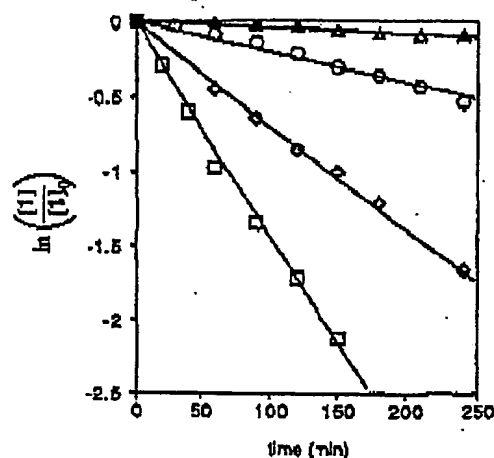


Figure 2. $\ln([1]/[1]_0)$ vs reaction time for the reaction of 1 with carbon dioxide under atmospheric pressure at 100 °C using NaBr (□), NaI (◊), NaCl (○), and NaOAc (Δ) as catalysts.

Table I. Apparent Rate Constant (k') and Yield of 2 of the Reaction of 1 and Carbon Dioxide under Atmospheric Pressure

catalyst (mol %)	k' (min ⁻¹) × 10 ⁴ ^a	yield of 2 (%) ^b
NaCl (5) ^c	20.2	41
NaBr (5)	155	98
NaBr (1)	27.4	48
NaBr (8)	95.2	88
NaBr (10)	217	100
NaI (5)	68.9	81
AcONa (5)	3.98	9
NaCN (5)	0	0
TbONa (5)	<1.0	1
NaClO ₄ (5)	0	0
NaCl (5) + 3 (7.5) ^c	14.9	30
NaBr (5) + 3 (7.5)	141	96
LiCl (5) ^c	46.2	66
LiBr (5)	295	100
LiI (5)	101	91
LiOPh (5)	<1.0	1
LiSPH (5)	<1.0	2
PhCH ₂ N ⁺ Me ₃ F ⁻ (5)	8.34	19
PhCH ₂ N ⁺ Me ₃ Cl ⁻ (5)	176	100
PhCH ₂ N ⁺ Me ₃ Br ⁻ (5)	31.9	57
PhCH ₂ N ⁺ Me ₃ I ⁻ (5)	7.12	17

^a In NMP at 100 °C. ^b Yield of 2 in the reaction for 4 h estimated from HPLC. ^c Catalyst was suspended.

$$-\frac{d}{dt}[1] = k'[1] \quad (1)$$

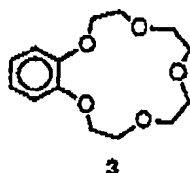
where [1] is the concentration of 1, t is reaction time, and k' is the apparent rate constant of the reaction. Integration of eq 1 gave eq 2:

$$\ln\left(\frac{[1]}{[1]_0}\right) = -k't \quad (2)$$

where [1]₀ is initial concentration of 1. $\ln([1]/[1]_0)$ was plotted a function of t in Figure 2. Since a linear relationship was observed in every case, the oxirane-CO₂ reaction seems to be first order with respect to the concentration of oxirane as expressed in eq 1, and k' can be a parameter of activity of a catalyst. k' values were estimated from the slope of the lines in Figure 2 and are summarized in Table I. Sodium halide (bromide and iodide) exhibited higher activity, while other sodium salts were found to show only a very low activity. Thus, sodium chloride was also examined as catalyst in spite of its

insolubility in NMP. Indeed, a simple first order kinetic was observed, and it showed a medium activity depicted in Table I.

Since crown ethers are known to enhance the solubility of alkali metal salts in organic solvents, 7.5 mol % (1.5 equiv to NaCl) of benzo-15-crown-5 (**3**), which exhibits a high affinity to sodium ion,²⁷ was added to the system with sodium chloride. However, sodium chloride did not dissolve completely in NMP (*N*-methylpyrrolidinone) in the presence of **3**, and k' decreased. Furthermore, **3** was added to the system with sodium bromide although k' also decreased. Thus, it can be concluded that crown ether acted as deactivator of the catalyst.



To evaluate the role of the cation part of the catalysts, a series of lithium compounds including iodide, bromide, chloride, phenolate, and thiophenolate was examined. In each case, the yield of **2** corresponded to the conversion of **1**, and no byproduct could be detected by HPLC analysis. A linear relationship between $\ln([1]/[1]_0)$ and t was observed, and the values of k' are summarized in Table I. Lithium salts showed higher activity in comparison with the corresponding sodium catalysts. Only halides showed a considerable catalytic activity, and bromide was more active than iodide, as in the case of the sodium salts. Unfortunately, lithium chloride precipitated during the reaction. Although simple first-order kinetics were observed for lithium chloride and the apparent activity was lower than that of bromide and iodide, its intrinsic activity could not yet be exactly determined.

Since quaternary ammonium salts dissolve in NMP, a series of benzyltrimethylammonium halides, including fluoride, chloride, bromide, and iodide, was used as catalyst to demonstrate the intrinsic order of the halide activity. In every case, the reaction system remained homogeneous during the reaction. The yield of **2** corresponded to the conversion of **1**, and no byproduct could be detected by HPLC analysis. A linear relationship between $\ln([1]/[1]_0)$ and t was observed, and the values of k' were calculated and are summarized in Table I. The catalytic activity of ammonium salts is rather low compared with the corresponding alkali metal salts.² It can be clearly shown that the intrinsic order of activity of the catalysts is chloride > bromide > iodide ~ fluoride.

To evaluate the kinetic order with respect to the catalyst, $\ln(k')$ obtained from an NaBr-catalyzed system was plotted as function of $\ln([NaBr])$ as shown in Figure 3. Since the slope of the line is 1.0, the oxirane- CO_2 reaction seems to be first order with respect to the concentration of the catalyst. On the other hand, the carbon dioxide pressure showed no effect on the yield of **2** at all, as shown in Figure 4. Consequently, the reaction rate can be expressed by following equation:

$$-\frac{d}{dt} [1] = k[1][cat.] \quad (3)$$

where $[cat.]$ is the concentration of the catalyst and the reaction rate is independent of the carbon dioxide pressure.

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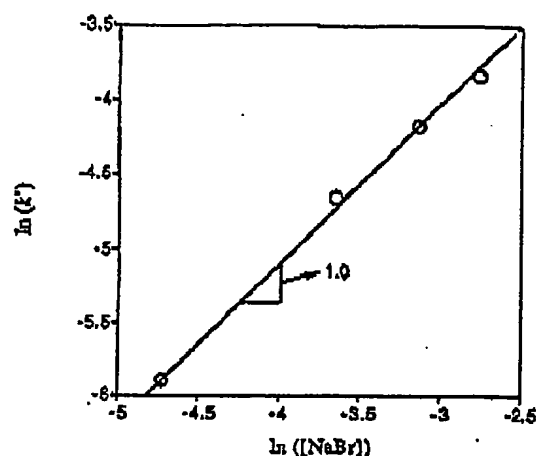


Figure 3. Plot of the rate constant (k') at 100 °C for the reaction of **1** with carbon dioxide under atmospheric pressure catalyzed by NaBr as a function of concentration of NaBr.

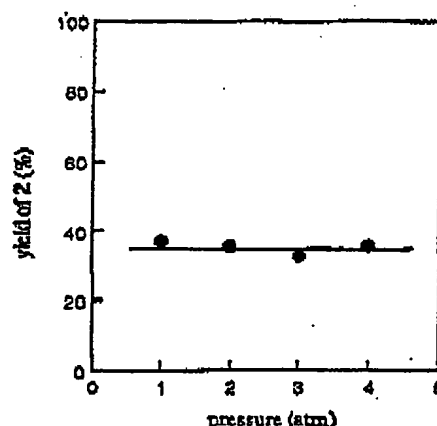


Figure 4. Yield of **2** vs pressure of carbon dioxide for the reaction of **1** with carbon dioxide at 100 °C for 30 min using NaBr as a catalyst.

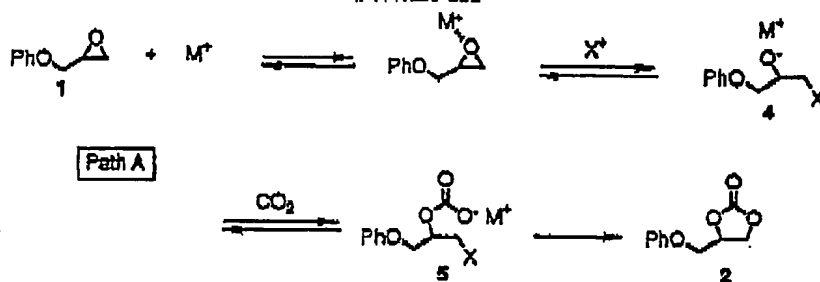
Discussion

Structure-Activity Relationship of the Catalyst.

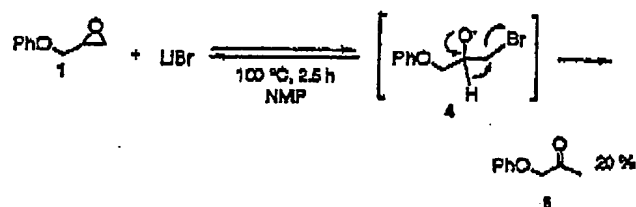
The counter anion of the salts significantly affects the catalytic activity. Essentially, only halides showed a considerable activity, probably because halide anions exhibit moderate nucleophilicity and high leaving ability. Salts with nonnucleophilic anions, such as *p*-toluenesulfonate and perchlorate, showed no activity in spite of higher leaving ability. Furthermore, salts with higher nucleophilic anions, such as acetate, cyanide, phenolate, and thiophenolate, showed very low activity probably because of low leaving ability. Rokicki et al. reported that potassium phenolate and acetate exhibited considerable catalytic activity at 40 atm,¹² indicating that such highly nucleophilic anions can catalyze the oxirane- CO_2 reaction via a different reaction mechanism under higher pressure.

The order of the activity of halides can be estimated to be chloride > bromide > iodide ~ fluoride. The apparently lower activity of sodium and lithium chloride may arise from the low solubility of these salts. Although the nucleophilicity of an anion depends on the solvent used, the order of the nucleophilicity of halides in S_N2 -type reactions in aprotic solvents, such as NMP, is known to

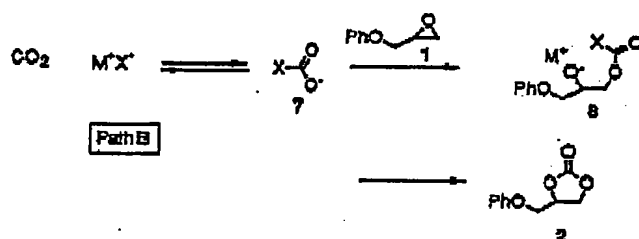
Scheme III



Scheme IV



Scheme V



be $\text{Cl}^- > \text{Br}^- > \text{I}^-$.²⁸⁻³⁰ Thus, the order of activity of halide anions is consistent with the order of nucleophilicity. The low activity of fluoride can be explained by its low leaving ability.²² The importance of anion nucleophilicity indicates that the rate-determining step of the oxirane-CO₂ reaction involves nucleophilic attack of an anion to oxirane, which is consistent with the kinetic analyses (eq 3).

Furthermore, the role of the catalyst cation is notable. In both series of bromide and iodide, the order of the activity is lithium salt > sodium salt > benzyltrimethylammonium salt. This order is in accord with the order of Lewis acidity of the cation,³¹ indicating the cation acted as Lewis acid to activate the oxirane.^{32,33} Since the Lewis acidity of cation decreases in the presence of a strong ligand, the catalyst activity decreased by addition of crown ether,³⁴ although the coordination ability of crown ether in NMP is very low.³⁵

Mechanistic Aspects. Although the reaction mechanism shown in Scheme III (path A) has been proposed for the oxirane-CO₂ reaction by many researchers,^{12,18,28} no reliable evidence has yet been reported. Path A was, however, clearly confirmed from kinetic analyses made in

our simple system. It was found that the rate-determining step is the attack of the anion part of the catalyst to oxirane. The importance of Lewis acidity of the cation part and nucleophilicity of the anion part of the catalyst as described above can be explained by this mechanism.

To prove the reaction of oxirane and salts, the reaction of 1 with 1 equiv of LiBr was carried out in the absence of CO₂ at 100°C for 2.5 h in NMP. 1-Phenoxy-2-propanone (6) was isolated in 20% yield as the sole product. 4 could not be detected because it cyclized rapidly to 1 and LiBr. Since the formation of 6 is reasonably explained by hydride transfer of 4 as shown in Scheme IV, the presence of key intermediate 4 was proved indirectly. Although the Lewis acid-catalyzed rearrangement of oxirane to aldehyde via more stable carbenium intermediate is well-known,^{36,37} the rearrangement of oxirane to ketone is not conventional. Formation of ketone 6 clearly indicates the attack of bromide anion to oxirane on the less substituted carbon regioselectively, which is characteristic of S_N2-type nucleophilic attacks on oxirane ring systems.³⁷

Although anions with higher nucleophilicity react with oxiranes more rapidly, acetate, phenolate, and thiophenolate anions may show no catalytic activity based on path A because of their low leaving ability in S_N2-type reaction on sp³ carbons. However, a small amount of 2 was obtained using these salts, and carboxylate and phenolate are known to catalyze the oxirane-CO₂ reaction in the presence of crown ether under high pressure conditions.¹² These facts indicate the possibility of another reaction mechanism, especially under high pressure. Because the catalytic activity of these highly nucleophilic anions seem to depend on the CO₂ pressure and these anions are good leaving groups in displacement reactions on carbonyl carbon, another possible reaction mechanism can be proposed as represented in Scheme V (path B). Since the equilibrium of the first step of path B with atmospheric pressure of CO₂ lies so far to the left, path B can not be the main reaction path under atmospheric pressure. However, when the pressure of CO₂ increases, the equilibrium may shift to the right so that the oxirane-CO₂ reaction via path B may proceed smoothly. At present, it is not clear whether halide salts can catalyze the oxirane-CO₂ reaction via path B.

Summary

We demonstrated the structure-activity relationship of the catalyst and a proposed reaction mechanism of the oxirane-CO₂ reaction by which CO₂ can be easily introduced into organic molecules under atmospheric pressure. Alkali metal salts, which have been thought to exhibit

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rather low catalytic activity in comparison with lipophilic onium salts, are more active catalysts for the oxirane- CO_2 reaction because alkali metal cations behave as Lewis acids. Furthermore, halides are the most suitable anion part of the catalyst for the oxirane- CO_2 reaction because of their appropriate nucleophilicity and leaving ability. Consequently, alkali metal halides were the best catalysts examined. A significant feature of the oxirane- CO_2 reaction is that the rate of the reaction is independent of the pressure of CO_2 because the reaction of alkoxide anion with CO_2 is rapid enough. Although we used **1** as a representative oxirane, these structure-activity relationships and reaction mechanism are assumed to be valid for most oxiranes.

The fact that easily available alkali metal salts act as highly active catalysts in nature is very important from an economical and practical viewpoint, although low solubility of alkali metal salts in organic solvents is disadvantageous. Further research of novel catalysts which combine lipophilicity, high Lewis acidity, high nucleophilicity, and high leaving ability is in progress.

Experimental Section

General Method. ^1H and ^{13}C NMR spectra were recorded on a JEOL PMX-60 SI (60 MHz) or on a JEOL EX-90 (90 MHz) spectrometer, using TMS as an internal standard. IR spectra were recorded on a JEOL JIR-5800 instrument. HPLC analyses were made by using UV detector (JASCO UVIDEC-100-V) at 245 nm, utilizing freshly distilled dichloromethane as solvent (elution rate; 1 mL/min, at room temperature), and a Gasukuro Kogyo Unisil Q 60-5 column.

Materials. 2,3-Epoxypropyl phenyl ether (**1**) and *N*-methylpyrrolidinone (NMP) were distilled from CaH_2 and stored under nitrogen. THF was distilled from sodium-benzophenone ketyl under nitrogen atmosphere before use. Naphthalene was recrystallized from ethanol. Benzo-15-crown-5 was recrystallized from *n*-hexane. Reagent grade phenol and thiophenol were used without further purification. Hydrated benzyltrimethylammonium fluoride was commercially available and was dried under vacuum at 100°C for 24 h over P_2O_5 , followed by crushing and subsequent further drying under vacuum at 100°C for 24 h over P_2O_5 before use. Other ammonium salts and inorganic chemicals were reagent grade and used after drying under vacuum.

Lithium Phenoxide. To a solution of 2.8 g (30 mmol) of phenol in 60 mL THF was added 18 mL of a 1.62 mol/L hexane

solution of butyllithium (30 mmol) dropwise under nitrogen at 0°C . After 30 min, the volatiles were removed under vacuum to obtain lithium phenoxide as a white powder.

Lithium Thiophenoxide. To a solution of 0.55 g (5 mmol) of thiophenol in 10 mL of THF was added 3.1 mL of a 1.62 mol/L hexane solution of butyllithium (5 mmol) dropwise under nitrogen at 0°C . After 30 min, the volatiles were removed under vacuum to obtain lithium thiophenoxide as a white powder.

4-(Phenoxymethyl)-1,3-dioxolan-2-one (2). A solution of 1.71 g (11 mmol) of **1** and 75 mg (0.5 mmol) of sodium iodide in 11 mL of NMP was heated at 100°C for 24 h under a carbon dioxide atmosphere. The reaction mixture was poured into 100 mL of water and precipitates were washed thoroughly with water. The crude cyclic carbonate was recrystallized in ethanol to obtain 1.61 g (73%) of 4-(phenoxymethyl)-1,3-dioxolan-2-one (**2**). *mp*: 98.5–99.5 $^\circ\text{C}$ (lit.³⁸ *mp* 98–99 $^\circ\text{C}$). NMR: (60 MHz, CDCl_3) δ 7.40–6.65 (m, 5H, Ar), 5.24–4.67 (m, 1H, CH), 4.62–3.87 (m, 4H, CH₂). IR: (KBr) 1805, 1167, 1092, and 780 cm^{-1} .

Reaction of 1 and Carbon Dioxide. A mixture of 1.50 g (10 mmol) of **1**, 5.0 mmol of catalyst, and 0.128 g of naphthalene was introduced in a two-necked flask equipped with a rubber septum. After the atmosphere was replaced with CO_2 , 10.0 mL of NMP was introduced using a syringe through a rubber septum to dissolve the mixture. The total volume of the solution became 11.4 mL. The solution was allowed to stand at 100°C with continuous stirring. Periodically, a small portion of the reaction mixture was removed out through rubber septum, diluted with dichloromethane, and washed with water. The organic extract was analyzed by HPLC to estimate the conversion of **1** and yield of **2** using naphthalene as an internal standard.

Reaction of 1 and LiBr. A solution of 782 mg (5.2 mmol) of **1** and 449 mg (5.2 mmol) of lithium bromide in 5 mL of NMP was heated at 100°C for 2.5 h under a nitrogen atmosphere. The reaction mixture was poured into 50 mL of phosphate buffer (pH = 6.8) and extracted with 5×10 mL of ether. The organic layer was washed with water and dried with MgSO_4 before evaporation. 1-Phenoxy-2-propanone (**6**) (158 mg, 20%) was isolated as the sole product from the crude mixture by preparative TLC (eluent: CH_2Cl_2). NMR: (60 MHz, CDCl_3) δ 7.43–6.61 (m, 5H, Ar), 4.46 (s, 2H, CH₂), 2.20 (s, 3H, CH₃). IR: (NaCl) 1736, 1722, 1599, 1589, 1497, 1228, 1171, 754, and 692 cm^{-1} .

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Ionic conductivity of highly deproteinized natural rubber having epoxy group mixed with alkali metal salts

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Abstract

The ionic conductivity of highly deproteinized liquid natural rubber having epoxy group (LEDPNR) mixed with alkali metal salts was investigated through impedance analysis to clarify the effect of proteins present in the rubber. The LEDPNR, thus used, was prepared from depolymerization of epoxidized natural rubber (ENR) latex, which was deproteinized by incubation of the latex with proteolytic enzyme and surfactant. The ionic conductivity of the resulting LEDPNR was dependent upon the alkali metal salts, where the ionic conductivity of LEDPNR/bis(trifluoromethane sulfonyl)imide (LiTFSI) was higher than that of LEDPNR/lithium perchlorate (LiClO₄). The difference in the ionic conductivity was attributed to the solubility of the salts through both high-resolution solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy and measurements of spin-lattice relaxation time. The ionic conductivity of LEDPNR/LiTFSI was also dependent upon concentration of LiTFSI and the conductivity reached the highest value at 20 wt.%, which was different from the monotonic increase in the ionic conductivity of liquid ENR prepared from untreated natural rubber latex.

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Keywords: Deproteinized natural rubber; Liquid epoxidized natural rubber; LiTFSI; Polymer electrolyte; Ionic conductivity

1. Introduction

Solid polymer electrolytes (SPEs) are widely recognized to be important materials to fabricate ionic devices such as polymer batteries, because they provide an effective conduction path of carrier ions like Li⁺ ion [1–3]. Substantial effort has been devoted to improve the ionic conductivity of the SPE with respect to the amount of charge carrier and mobility of the ions [4]. For instance, to increase the ionic conductivity, it is necessary to optimize the amount of charge carrier and mobility of ions, since the excess amount of charge carrier results in decrease in the mobility [5–7]. In this regard, low glass transition temperature, T_g , and melting temperature, T_m , are required for the SPE, even though it contains polar substituents that resulted in higher T_g and T_m . In the last

two decades [8–11], oligomer electrolytes were prepared to reduce T_g and T_m . However, the resulting oligomer was mechanically unstable, so that it spread out after preparing an as-cast film. It is thus quite important to use a polar rubbery material as a conducting medium, because it has not only polar substituents to transport Li⁺ but also low T_g to enhance the mobility.

In the previous work [12], a commercial epoxidized natural rubber (ENR) after mastication was proposed as a polymer electrolyte, in which the ionic conductivity increased monotonically, as the salt concentrations increased: for instance, about 10^{-4} S cm⁻¹ at 60 wt.% salt. However, the monotonic increase in the ionic conductivity was suggested to be different from the normal dependence of the ionic conductivity of the polymer electrolyte on the salt concentrations, in which the maximum was shown at the adequate salt concentration, except for the presence of water [13,14]. Thus, the monotonic increase in the ionic conductivity against the salt concentrations may imply the presence of water that causes serious problems such as dendrite formation in the electrolyte and corrosion of electrode.

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Since natural rubber contains about 2 wt.% proteins that are attractive with water [15,16], it is quite important to remove the proteins from the rubber.

In our previous work [17], we proposed highly deproteinized natural rubber and hyper-deproteinized natural rubber, which contained about 0.1 and 0.02 wt.% proteins, respectively, being less than about 2 wt.% proteins present in the untreated natural rubber. An epoxidized liquid rubber prepared from the deproteinized natural rubbers was adopted as a polar rubbery electrolyte that contained fewer amounts of proteins. It may be an important and useful polymer electrolyte, since natural rubber is one of metabolic materials produced in *Hevea brasiliensis*.

In the present work, to evaluate the liquid rubber as a polymer electrolyte, we measured the ionic conductivity for the mixtures of liquid epoxidized natural rubber with lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) or lithium perchlorate (LiClO₄) by a.c. impedance. The interactions between the liquid rubber and salts were investigated through high-resolution solid-state ¹³C NMR spectroscopy and measurement of spin-lattice relaxation time.

2. Experimental

2.1. Sample preparation

The rubber used in this study was high ammonia natural rubber (NR) latex, which was supplied by Sumitomo Rubber Industries, Japan. Deproteinization of the rubber latex was made by incubation of the latex with 0.04 wt.% proteolytic enzyme (Kuo, KP-3939) and 1 wt.% sodium dodecyl sulfate (SDS) for 12 h at 305K followed by centrifugation [17]. The cream fraction was re-dispersed into 1 wt.% SDS solution and washed twice by centrifugation to prepare deproteinized natural rubber (DPNR) latex.

NR and DPNR, pre-cooled at 283K, were epoxidized in the latex stage with fresh peracetic acid (33 wt.% concentration) for 3 h at pH 5–6. After completion of the reaction, the pH of the solution was adjusted to 7.1.

Depolymerization of the epoxidized rubber was carried out by incubation of the latex with ammonium persulfate ((NH₄)₂S₂O₈) and propanal at 338 K for 12 h. The resulting latex was coagulated with methanol followed by purification with toluene and methanol, and dried at 303 K for a week under reduced pressure. Nitrogen content, X_{nitrogen} , epoxy group content, X_{epoxy} , glass transition temperature, T_g , weight average molecular weight, M_w , number average molecular weight, M_n , and polydispersity, M_w/M_n for NR and DPNR, liquid epoxidized DPNR (LEDPNR) and liquid epoxidized NR (LENR) are tabulated in Table 1. The structure of the LENR and LEDPNR were characterized by ¹H NMR Spectroscopy [18].

The LEDPNR and LENR were mixed with salts to prepare polymer salt electrolyte film. Salts used in the

Table 1
Characteristics of NR, DPNR, LEDPNR and LENR

Specimen	X_{epoxy} (mol%)	X_{nitrogen} (wt%)	T_g (K)	M_n (10 ³)	M_w (10 ³)	M_w/M_n
NR	—	0.340	212	3.37	25.10	7.45
DPNR	—	0.017	213	2.10	17.80	8.48
LEDPNR	33	—	241	0.18	0.41	2.20
LENR	29	—	238	0.38	1.21	3.19

present study were lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) and lithium perchlorate (LiClO₄). LiTFSI was gifted by Sumitomo 3M and LiClO₄ was purchased from Aldrich. The rubbers after drying for at least a week were dissolved in dried tetrahydrofuran. The solution was mixed with the salts followed by casting onto Teflon sheets to prepare film specimens for the measurement of ionic conductivity. The resulting film was dried under reduced pressure at 323 K for 24 h.

2.2. Measurements

Measurements of molecular weight and molecular weight distribution of the rubber were made by a TOSOH gel permeation chromatography, consisting of a TOSOH CCPD pump, a RI-8012 Differential Refractometer and a UV-8011 UV detector. The measurement was made at room temperature and the flow rate of the mobile phase, THF, was 0.5 ml/min. The molecular weights were estimated on the basis of the molecular weight of standard polystyrene.

¹H NMR measurement was carried out with a JEOL EX-400 NMR spectrometer at the pulse repetition time of 7 s for 45° pulse. The rubber was dissolved in deuterated chloroform. The epoxy group content was estimated from intensity ratio of the characteristic signals at 2.7 and 5.1 ppm, respectively. Measurements of high-resolution solid-state ¹³C NMR and spin-lattice relaxation time, T_1 , were made with a JEOL GX-270 NMR spectrometer. The usual 180°-τ-90° pulse sequence with a repetition time of 5 × T_1 was applied to the T_1 measurement. The measurement was made with decay times, τ, ranging from 1 to 5000 ms, and 180 scans [19].

DSC measurements were made with a Seiko Instrument DSC 220 differential scanning calorimeter over the temperature range of 153–373 K at the heating rate of 10 K/min. Rubber samples of about 10 mg were encapsulated in an aluminum pan. The midpoint temperature was used as the T_g of the sample.

The ionic conductivity was measured by the complex impedance method with Schlumberger Solartron-1260 impedance gain-phase analyzer in the frequency range from 10 to 10⁶ Hz. The ionic conductivity was measured during cooling with the cooling rate of 3 K/min from 333 to 283 K. The impedance data were collected by the custom-designed apparatus and depicted as Arrhenius plots of the ionic conductivity [20]. The sample cell preparation and

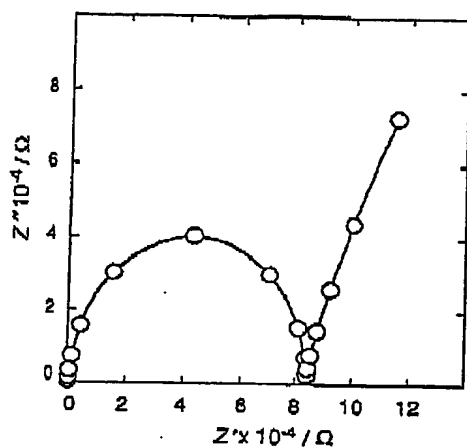


Fig. 1. Cole-Cole plot for LEDPNR mixed with 20 wt.% LiTFSI at 323 K.

measurements were performed in a glove box filled with dry nitrogen gas.

3. Results and discussion

A typical Cole-Cole plot for a mixture of LEDPNR with 20 wt.% LiTFSI (LEDPNR/LiTFSI) at 323 K is shown in Fig. 1. The imaginary part of impedance, Z'' , was dependent upon the real part, Z' , which drew a locus of a half circle, as in the case of the mixture of poly(ethylene oxide) (PEO) with alkali metal salts [21]. Thus, the bulk resistance (R_b) was estimated from a point of intersection of the curve and the axis of abscissa [22,23]. The

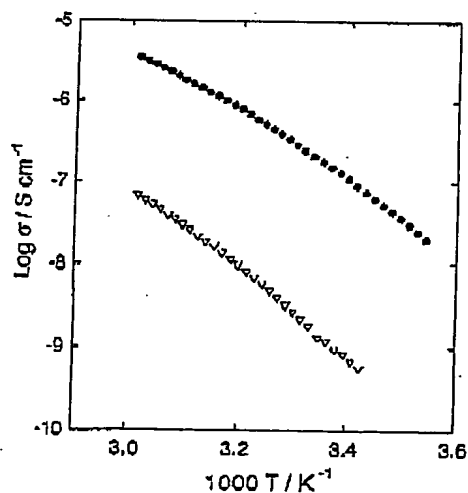


Fig. 2. Temperature dependence of the ionic conductivity for the mixtures of LEDPNR with salt: (●), LiTFSI and (○), LiClO₄ in a ratio of 80:20 by mole, respectively.

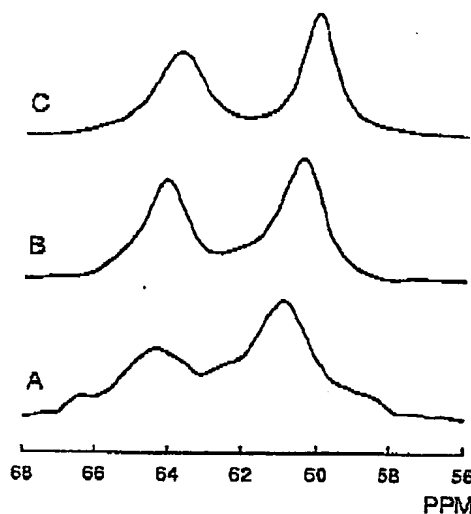


Fig. 3. High-resolution solid-state ¹³C NMR spectra at 323 K: (A) LEDPNR/LiTFSI; (B) LEDPNR/LiClO₄; (C) LEDPNR.

ionic conductivity, σ , was estimated from the value of R_b as follows:

$$\sigma = \frac{d}{R_b A}$$

where d is the thickness of the film specimen and A the area of the electrode. The estimated values of σ for LEDPNR/LiTFSI or LEDPNR/LiClO₄ are plotted against a reciprocal temperature, $1/T$, in Fig. 2. The σ in Fig. 2 increased monotonically with decreasing $1/T$, reflecting that σ was a function of the mobility of LEDPNR. Furthermore,

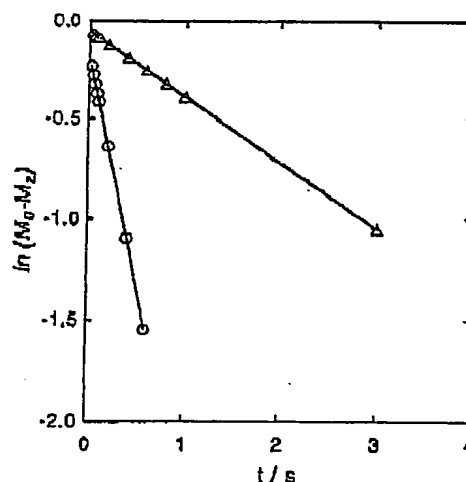


Fig. 4. Typical plot of $\ln(M_0 - M_2)$ versus time for LEDPNR/LiTFSI at 323 K: (Δ) C₆₀ ppm; (○) C₆₀ ppm.

Table 2
 T_1 of Li^+ salt containing LEDP NR

Specimen	T_1 values at 323 K (s)	
	C_{60} ppm	C_{64} ppm
LEDPNR/LiTFSI	3.2	0.5
LEDPNR/ LiClO_4	3.5	1.2

at each temperature, the value of σ for LEDP NR/LiTFSI was found to be higher than that for LEDP NR/ LiClO_4 .

To investigate the difference in σ between LEDP NR/LiTFSI and LEDP NR/ LiClO_4 in a view of the interaction between epoxy group and salt, high-resolution solid-state ^{13}C NMR measurement was carried out for the mixtures. The ^{13}C NMR spectra for LEDP NR/LiTFSI and LEDP NR/ LiClO_4 , ranging from 56 to 68 ppm, are shown in Fig. 3. The signals at 60 and 64 ppm, respectively assigned to tertiary and quaternary carbons of epoxy group [24], moved to lower magnetic field, that is, larger value of chemical shift, after mixing LEDP NR with the salts. The shift of the signals was more significant as LEDP NR was mixed with LiTFSI, rather than LiClO_4 . Since the cation used in the present study was Li^+ , the significant shift of the signals for LEDP NR/LiTFSI may be associated with the amount of Li^+ that interacts with the epoxy group.

The difference in the amount of Li^+ that interacts with the epoxy group between LEDP NR/LiTFSI and LEDP NR/ LiClO_4 must reflect the half width of the signals at 60 and 64 ppm. The half width of the signal at about 64 ppm for LEDP NR, LEDP NR/ LiClO_4 and LEDP NR/LiTFSI were about 70, 100 and 170 Hz, respectively. The larger value of the half width for LEDP NR/LiTFSI may be due to overlapping of the signals according to various chemical conditions of the epoxy groups that interact with Li^+ , whereas the smaller value for LEDP NR/ LiClO_4 may be

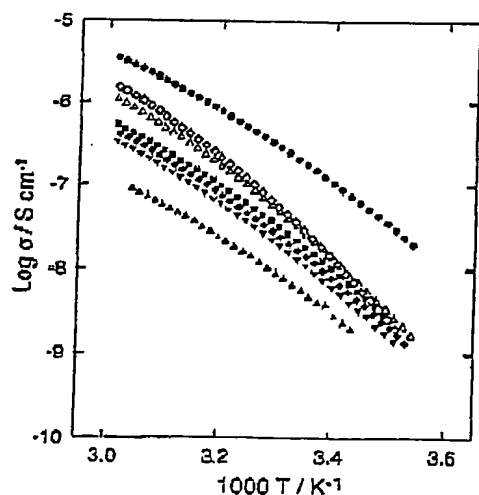


Fig. 5. Temperature dependence of the ionic conductivity for LEDP NR/LiTFSI at the various concentrations of LiTFSI: (○) 50 wt.%; (△) 30 wt.%; (●) 20 wt.%; (◆) 15 wt.%; (■) 10 wt.%; (▼) 5 wt.%; (▲) 3 wt.%.

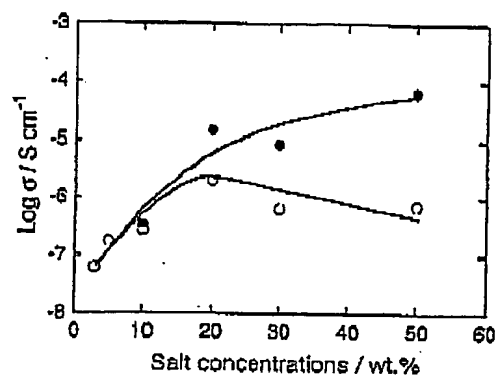


Fig. 6. Ionic conductivity for (○) LEDP NR/LiTFSI and (●) LEDP NR/ LiClO_4 as a function of salt concentrations.

due to a few conditions. The difference in the half width may arise from the solubility of the salts, since the conditions may be associated with the amount of Li^+ ; the larger the amount of Li^+ , the greater the condition is.

To assure the difference in the solubility between LiClO_4 and LiTFSI, spin-lattice relaxation time, T_1 , was measured through ^{13}C NMR spectroscopy. Fig. 4 shows a typical plot of $\ln(M_0 - M_z)$ versus time, t , for LEDP NR/LiTFSI at 323 K, where M_0 is the macroscopic magnetization and M_z the longitudinal component of the macroscopic magnetization. The T_1 was estimated from the slope of the straight line of the plot. The estimated values of T_1 for LEDP NR/LiTFSI and LEDP NR/ LiClO_4 are tabulated in Table 2. The T_1 for LEDP NR/LiTFSI was shorter than that for LEDP NR/ LiClO_4 , even though the molar ratio of the salts to oxygen atom in the mixtures was the same, i.e., $\text{Li}/\text{O} \approx 0.178$. This may be attributed to the difference in the amount of free Li^+

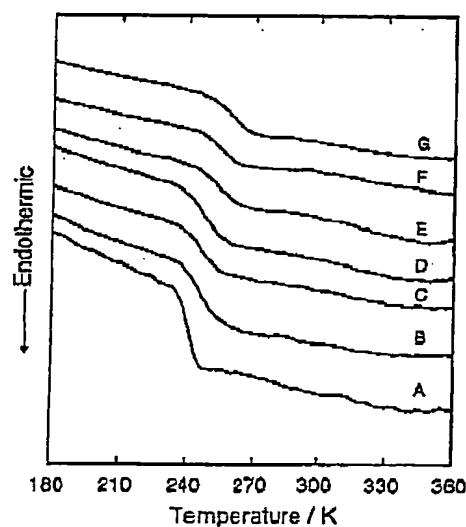


Fig. 7. DSC thermograms for LEDP NR/LiTFSI at various concentrations of salt: (A) 0 wt.%; (B) 5 wt.%; (C) 10 wt.%; (D) 15 wt.%; (E) 20 wt.%; (F) 30 wt.%; (G) 50 wt.%.

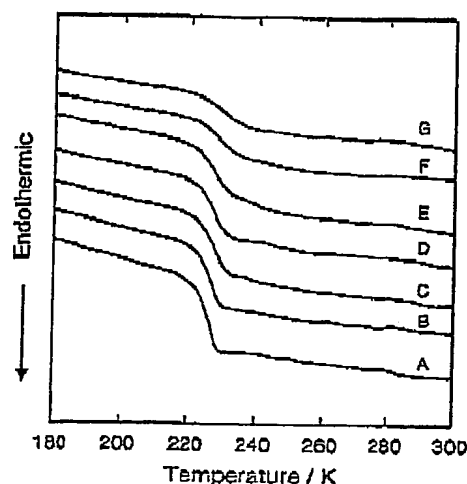


Fig. 8. DSC thermograms for LENR/LiTFSI at various concentrations of salt: (A) 0 wt.%; (B) 5 wt.%; (C) 10 wt.%; (D) 15 wt.%; (E) 20 wt.%; (F) 30 wt.%; (G) 50 wt.%.

due to the solubility of the salt that is dependent upon a lattice energy of the salt. Thus, LiTFSI was found to be a suitable salt for forming a polymer electrolyte with LEDPNR.

The Arrhenius plots of σ for mixtures of LEDPNR with various concentrations of LiTFSI are shown in Fig. 5. The σ for all of LEDPNR/LiTFSI increased monotonically as $1/T$ decreased; Furthermore, the values of σ were approximately similar to each other, and the slope of the line was apparently independent of the concentrations of LiTFSI. To clarify the effect of salt concentrations on σ , plots of σ at 323 K versus concentrations of LiTFSI are shown in Fig. 6. The σ was dependent on the concentrations of LiTFSI and reached the maximum at 20 wt.%, that is, $\text{Li}/\text{O} = 0.178$. The increase in σ at lower concentrations of LiTFSI is attributed to the increase in the amount of Li^+ . On the other hand, the decrease in σ at higher concentrations of LiTFSI may be due to the constraint of the segmental motion of LEDPNR. To confirm the constraint of the segmental motion, a glass transition temperature, T_g , of the mixtures was measured. The DSC thermograms of LEDPNR/LiTFSI are shown in Fig. 7. The T_g of the mixtures rose as the concentrations of LiTFSI increased, attributable to the pseudo-crosslinkings of LEDPNR, as in the case of PEO/LiTFSI reported in the previous study [25].

In Fig. 6, the σ for mixtures of liquid epoxidized natural rubber (LENR) prepared from untreated natural rubber latex with various concentrations of LiTFSI is also shown as a control in order to emphasize the importance of the deproteinization of natural rubber. The σ for LENR/LiTFSI increased monotonically as the concentrations of LiTFSI increased, which was distinguished from σ for LEDPNR/LiTFSI, but similar to σ for the reported mixture of masticated ENR50 with lithium triflate [12]. This may be due to the residual proteins present in LENR, which is

known to be attracted with water. Fig. 8 shows DSC thermograms for the mixtures. The T_g for LENR/LiTFSI was independent of the concentrations of LiTFSI, which was quite different from the dependence of T_g on the LiTFSI concentration for LEDPNR/LiTFSI. The dependence of T_g of LENR on the concentrations of LiTFSI was similar to that reported in the previous work [12]. Since the difference between LEDPNR and LENR is only the amount of proteins that are contained in the rubbers, respectively, the monotonic increase in σ for LENR, different from that for LEDPNR may be due to the effect of the proteins. This demonstrates that, in order to investigate the Li^+ ion conduction for modified natural rubber, natural rubber will be subjected to the deproteinization to diminish the effect of the proteins on σ .

4. Conclusions

The Li^+ ion conduction of LEDPNR was dependent upon the type of salt, their concentrations and temperature. The ionic conductivity of LEDPNR/LiTFSI was higher than that of LEDPNR/ LiClO_4 . Based upon the chemical shift, half-width and spin-lattice relaxation time of ^{13}C NMR spectroscopy, LiTFSI was confirmed as a suitable salt for LEDPNR due to the high solubility, which resulted in high ionic conductivity. The mixture of LEDPNR with 20 wt.% LiTFSI showed the highest ionic conductivity, i.e., about $2.0 \times 10^{-6} \text{ S cm}^{-1}$ at 323 K, in which the ratio of the Li/O was 0.178. The ionic conductivity was also dependent upon the proteins that were contained in natural rubber. These results suggest that it may be important to remove the proteins from natural rubber to prepare the polymer electrolyte from the rubber.

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Ionic conductivity of highly deproteinized natural rubber having epoxy group mixed with alkali metal salts

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Abstract

The ionic conductivity of highly deproteinized
liquid natural rubber having epoxy group
(LEDPNR) mixed with alkali metal salts was
investigated through impedance analysis to
clarify the effect of proteins present in the rubber.

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NOTE

Preparation of Carbonated Natural Rubber

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INTRODUCTION

Carbonated natural rubber may be a novel functional organic material because it consists of flexible isoprene units and polar carbonate groups, as shown in Figure 1. It may be prepared from epoxidized natural rubber (ENR) with carbon dioxide because low-molecular-weight carbonated compounds have been prepared from alkyl oxirane with carbon dioxide in the presence of lithium bromide (LiBr) as a catalyst.^{1–4} The carbonation of alkyl oxirane has been proposed to proceed through an intermediate consisting of alkyl oxirane, carbon dioxide, and LiBr, followed by back-biting of $-OLi$ to $-CH_2Br$ to form cyclic carbonate groups, as shown in Scheme 1.⁴ According to the proposed mechanism, alkyl oxirane as a substrate must be close to carbon dioxide and LiBr to form the intermediate. Thus, to apply this reaction to ENR, it is necessary to make an interaction between the epoxy group of ENR and LiBr. However, proteins present in natural rubber prevent the interaction between the epoxy group and LiBr because the proteins are attracted with water.⁵ In fact, no publication has reported the preparation of carbonated natural rubber. Thus, to prepare carbonated natural rubber, we have to remove the proteins from natural rubber.

In previous works,^{6,7} we proposed the efficient purification procedure of natural rubber with urea as a denaturant because urea is known to change the conformations of proteins through hydrophilic interactions,

and it stabilizes the proteins in water because of hydrophobic interactions. The resulting deproteinized natural rubber (DPNR) was proved to contain less than 0.005 wt % nitrogen sources, corresponding to less than about 0.03 wt % proteins. From the DPNR, we prepared liquid deproteinized natural rubber having epoxy groups (LEDPNR), which was miscible with lithium salt.^{6,9} Because we found interactions between the epoxy group of LEDPNR and the lithium cation of the lithium salt in the mixture through solid-state ^{13}C NMR spectroscopy,⁹ the epoxy group may be attracted with Li salt because of the absence of water. Furthermore, supercritical carbon dioxide was reported to penetrate natural rubber,^{10,11} even though the rubber was vulcanized. Thus, after the swelling of the mixture with supercritical carbon dioxide, carbonated natural rubber may be prepared, as in the case of alkyl oxirane.⁴

Carbonated natural rubber may be characterized by not only Fourier transform infrared (FTIR) spectroscopy but also NMR spectroscopy. In the case of FTIR spectroscopy, a strong absorption peak characteristic of the cyclic carbonate group was reported to appear at

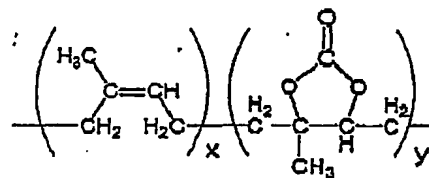
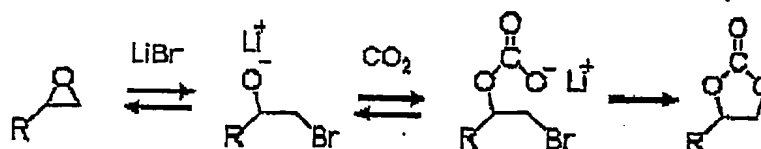


Figure 1. Chemical structure of carbonated natural rubber.

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Scheme 1. Proposed mechanism of carbonation for low-molecular-weight alkyl oxirane.

1780 cm^{-1} for the low-molecular-weight carbonated compound.¹² In contrast, the cyclic carbonate group may be positively proved by NMR spectroscopy with various pulse techniques, that is, two-dimensional NMR measurements including inverse correlations. Because ^1H - ^1H correlation, ^1H - ^{13}C correlation, and the correlation of ^1H - ^{18}O through two or more bonds [heteronuclear multiple bond correlation (HMBC)] are detected by two-dimensional NMR measurements, the presence of the carbonate group may be rationally confirmed by NMR spectroscopy, despite no reported assignment.

In this study, an attempt to prepare carbonated natural rubber from LEDP NR was made in the presence of supercritical carbon dioxide. The products were characterized with ^1H and ^{13}C NMR spectroscopy.

EXPERIMENTAL

The natural rubber latex used in this study was commercial high-ammonia natural rubber latex. The deproteinization of natural rubber was achieved by the incubation of the latex with 0.1 w/v urea (Nacalai Tesque; 99.5%) and 1.0 w/v sodium dodecyl sulfate (Kishida Reagents Chemicals Co., Ltd.; 99%) for 1 h at 303 K followed by centrifugation.^{6,7} The nitrogen content (N-content), number-average molecular weight (M_n), weight-average molecular weight (M_w), and M_w/M_n values for the resulting DP NR are tabulated in Table 1.

DP NR, precooled at 283 K, was epoxidized in the latex stage with fresh peracetic acid (concentration = 33 v/v) for 3 h at pH 5–6. After the completion of the reaction, the pH of the latex was adjusted to about 9 with an ammonia solution (Nacalai Tesque; 99.5%). The degradation of the resulting epoxidized DP NR was carried out by the incubation of the epoxidized DP NR latex with ammonium persulfate (Nacalai Tesque; 99.5%) and propanal (Nacalai Tesque;

99.5%) at 338 K for 10 h to prepare LEDP NR. The LEDP NR latex was coagulated with methanol (Nacalai Tesque; 99%), and this was followed by purification with toluene (Nacalai Tesque; 99.5%) and methanol; the coagulated LEDP NR was dried at 303 K for a week under reduced pressure.

The carbonation of LEDP NR was performed with supercritical carbon dioxide under various conditions. LEDP NR was dissolved in tetrahydrofuran (THF; Nacalai Tesque; 99.5%), and this was followed by mixing with LiBr. From the solution, an as-cast film was prepared and dried under reduced pressure for a week. The resulting as-cast film was placed in a high-pressure reactor and was reacted with supercritical carbon dioxide under the conditions shown in Table 2.

The procedure to prepare the carbonated DP NR is schematically represented in Figure 2.

The apparent molecular weights and molecular weight distribution (M_w/M_n) of the rubbers were determined with a gel permeation chromatography system from Tosoh, Ltd., with a computer control dual pump, an RI-8012 differential refractive-index detector, a UV-8011 ultraviolet spectroscopy detector, and a series of three G4000HXL columns (bead size = 5 μm , pore size = 10^4 Å) 300 mm long with a 7.8-mm i.d. THF was used as an eluent, and the flow rate was 0.5 mL/min at room temperature. Standard polystyrenes were used for a calibration.

FTIR measurements of the carbonated DP NR were performed with a Jasco FTIR-410 spectrometer at a resolution of 4 cm^{-1} .

NMR measurements were carried out with a JEOL ECA-400 NMR spectrometer operating at 399.65 and 100.4 MHz for ^1H and ^{13}C , respectively. The rubber was dissolved in chloroform- d . Chemical shifts were referred to tetramethylsilane (TMS). ^1H and ^{13}C NMR measurements were carried out at 323 K at the pulse repetition times of 7 and 5 s, respectively. Two-dimensional ^1H - ^1H correlation, ^1H - ^{13}C correlation, and HMBC measurements were made to collect two-dimensional hypercomplex data. After being weighted

Table 1. N-Content, X_{epoxy} , M_n , M_w , and M_w/M_n for DP NR and LEDP NR

Specimen	N-Content (w/w)	X_{epoxy} (mol %)	$M_n/10^5$ (g mol^{-1})	$M_w/10^5$ (g mol^{-1})	M_w/M_n
DP NR	0.02		2.1	17.8	8.5
LEDP NR	0.02	33.5	0.21	0.56	2.7

Table 2. Reaction Conditions and ξ

Catalyst	Catalyst Feed (mol/Epoxy)	Entrainer	Time (h)	Temperature (K)	Pressure (MPa)	ξ (%)
LiClO_4	0.1		6	373	14	— ^a
LiI	0.1		6	373	14	8.1
LiBr	0.1	THF	6	323	14	2.4
LiBr	0.1	THF	6	373	14	4.4
LiBr	0.1	Toluene	6	373	14	5.1
LiBr	0.1		6	323	14	2.6
LiBr	0.1		6	373	14	4.8
LiBr	0.1		6	403	14	— ^a
LiBr	0.1		6	403	20	7.2
LiBr	0.1		6	423	14	— ^a

^a Undetermined because of the gel fraction.

with a shifted sine-bell function, the data were Fourier-transformed in the absolute value mode.

RESULTS AND DISCUSSION

FTIR spectra for LEDPNR and carbonated DPNR are shown in Figure 3, in which normalized absorbance, A/A_0 , estimated from a ratio of peak intensity at

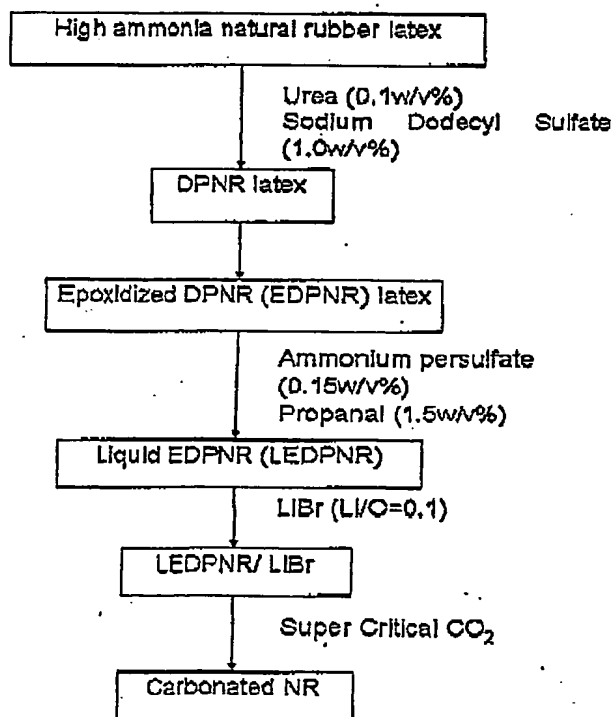


Figure 2. Schematic illustration of preparing carbonated DPNR.

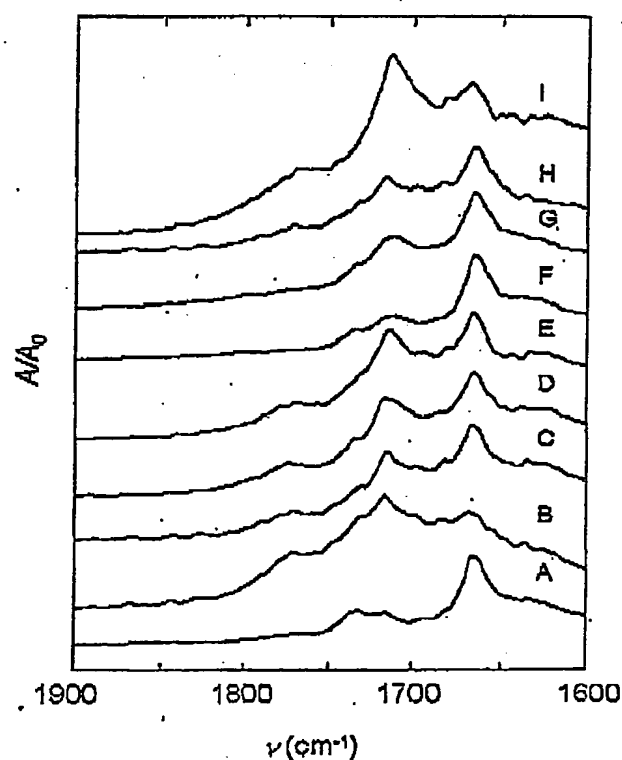


Figure 3. FTIR spectra for (A) LEDPNR, (B) carbonated DPNR prepared with LiI at 373 K and 14 MPa, (C) carbonated DPNR prepared with LiBr and THF at 323 K and 14 MPa, (D) carbonated DPNR prepared with LiBr and THF at 373 K and 14 MPa, (E) carbonated DPNR prepared with LiBr and toluene at 373 K and 14 MPa, (F) carbonated DPNR prepared with LiBr at 323 K and 14 MPa, (G) carbonated DPNR prepared with LiBr at 373 K and 14 MPa, (H) carbonated DPNR prepared with LiBr at 403 K and 14 MPa, and (I) carbonated DPNR prepared with LiBr at 403 K and 20 MPa.

1664 cm^{-1} , was delineated against wave number, ν . The characteristic region of the absorbance peaks of $>\text{C}=\text{O}$ and $>\text{C}=\text{C}<$ stretching vibrations is expanded. In the spectra, broad peaks appear around 1700–1750 and 1780 cm^{-1} , which have been attributed to ester, formyl, and carbonate groups.¹² The broad peaks increase in intensity as the reaction temperature increases. Because a formyl group has been reported to be formed by a side reaction during the carbonation of low-molecular-weight alkyl oxirane,¹³ the increase in the intensity of the peaks at 1700–1750 and 1780 cm^{-1} may demonstrate that not only carbonation but also side reactions occur in LEDPNR. To distinguish the carboxylic, formyl, and carbonate groups more exactly, NMR measurements were carried out.

Typical ^1H NMR spectra for DPNR and LEDPNR are shown in Figure 4. Signals characteristic of methyl, methylene, and unsaturated methine protons of isoprene units appear at 1.6, 2.1, and 5.1 ppm, respectively. After the epoxidation and depolymerization of DPNR, two other signals appear distinctly at 2.7 and 1.2 ppm, and they have been assigned to methine and methyl protons of the resulting epoxy groups, respectively. In Figure 4, small signals of a formyl group around 9.4 and 9.8 ppm are also shown for LEDPNR, as reported in our previous article.⁸ This implies that the broad peaks around 1700–1750 cm^{-1} in the FTIR spectra for LEDPNR may be attributed to not only ester linkages of linked fatty acid ester groups¹⁴ but also formyl groups.⁸

The epoxy group content (X_{epoxy}) was thus estimated from the intensity ratio of the signals:

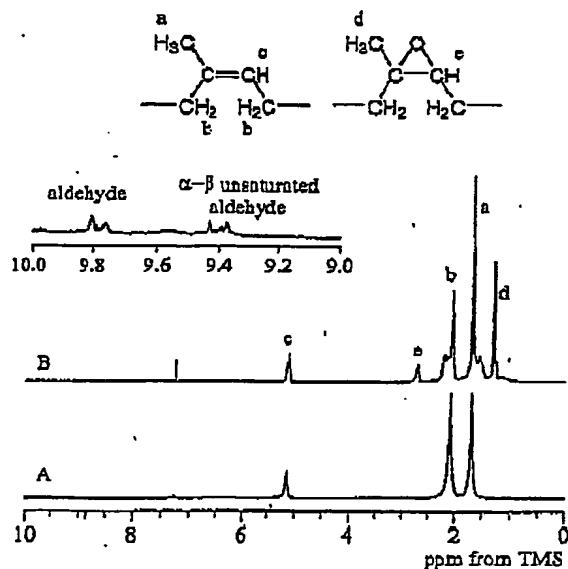


Figure 4. ^1H NMR spectra for (A) DPNR and (B) LEDPNR.

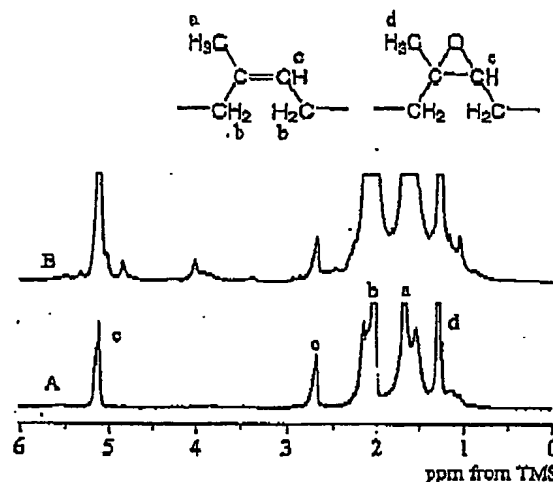


Figure 5. ^1H NMR spectra for (A) LEDPNR and (B) carbonated DPNR.

$$X_{\text{epoxy}} = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \times 100 \quad (1)$$

where I is the intensity of the signals and the subscripts represent chemical shifts. The estimated X_{epoxy} value of LEDPNR is tabulated in Table 1. X_{epoxy} was 33.5 mol %. In Table 1 are also shown M_n , M_w , and the polydispersity index (M_w/M_n) for LEDPNR. The values of M_n and M_w were about 2×10^4 and 5×10^4 , respectively, which were significantly less than the values of about 2×10^5 and 2×10^6 for DPNR. These are consistent with our previous results.^{8,9}

Figure 5 shows a typical ^1H NMR spectrum for a product obtained by the incubation of LEDPNR with supercritical carbon dioxide at 403 K and 20 MPa, together with the spectrum for LEDPNR. As for the product, two signals were newly found at 4.0 and 4.8 ppm in the ^1H NMR spectrum, which did not appear in the spectrum for LEDPNR. This may suggest the formation of cyclic carbonate groups for the product. To assign the signals, in Figure 6, the aliphatic region of the ^1H NMR spectrum for the product has been expanded, and it is compared with a corresponding spectrum for propylene carbonate as a model. For propylene carbonate, two signals at 4.0 and 4.6 ppm have been assigned to equatorial and axial methylene protons of cyclic carbonate groups^{15,16} due to interactions with $-\text{CH}_3$ and $-\text{H}$, respectively. Furthermore, the ^1H chemical shift of the cyclic carbonate group of 4,4,5-trimethyl-1,3-dioxolan-2-one as an additional model has been estimated to be 4.0 ppm, according to Furst's method,^{15,16} because of the interaction with $-\text{CH}_3$ and $-\text{CH}_2-$. Thus, the signal at 4.0 ppm for the carbonated DPNR shown in Figure 6 can be assigned to the methine proton of the cyclic carbonate group of the carbonated DPNR. This assignment is supported by ^1H – ^1H correlation measure-

NOTE 1565

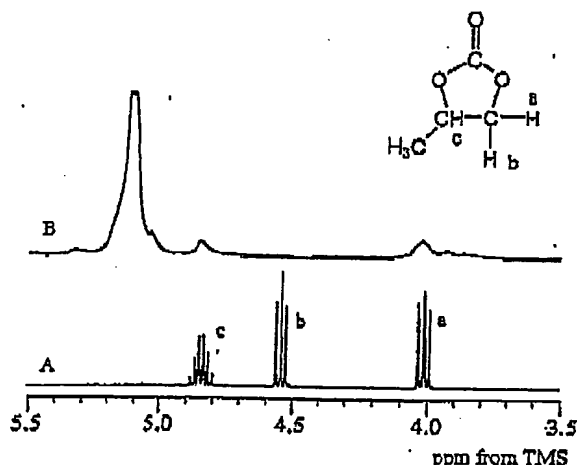


Figure 6. ^1H NMR spectra for (A) propylene carbonate and (B) carbonated DPNR.

ments of the carbonated DPNR. Two-dimensional ^1H - ^1H correlation spectra for the carbonated DPNR are shown in Figure 7, in which cross peaks appear because of spin coupling between ^1H and ^1H . The signal at 4.0 ppm is correlated to the methylene proton at about 1.5 ppm,¹⁵⁻¹⁷ which is a neighbor of the carbonate group. On the basis of the structure of the car-

bonated DPNR shown in Figure 1, it may be possible to assign the signal at 4.0 ppm to the methine proton of the cyclic carbonate group.

Figure 8 shows ^{13}C NMR spectra for LEDPNR, carbonated DPNR, and propylene carbonate. As for LEDPNR, two signals characteristic of the epoxy group are shown at 61 and 64 ppm in the spectrum, which have been assigned to quaternary and tertiary carbons of the epoxy group, respectively. However, no signal appears around 75 and 150 ppm. After carbonation, signals appear at 74, 75, and 151 ppm, whereas the intensity of the signals at 61 and 64 ppm decreases. The signals appearing at 74, 75, and 151 ppm have been assigned to quaternary ($>\text{C}<$), tertiary ($>\text{CH}-$), and quaternary ($-\text{O}-(\text{C}=\text{O})-\text{O}-$) carbons of the carbonate group, as shown in Figure 1, according to chemical-shift values of signals detected for propylene carbonate and those estimated for 4,4,5-trimethyl-1,3-dioxolan-2-one^{15,16} as a model.

To confirm the assignments of ^1H NMR and ^{13}C NMR spectra, ^{13}C - ^1H correlation and HMQC measurements were carried out for the carbonated DPNR. Figure 9 shows ^{13}C - ^1H correlation spectrum for the carbonated DPNR, in which cross peaks appear because of spin coupling between ^{13}C and ^1H in ^{13}C - ^1H correlation spectra. The ^{13}C signals for *cis*-1,4-isoprene units are rationally correlated to the corresponding ^1H signals. Furthermore, the ^{13}C signal at

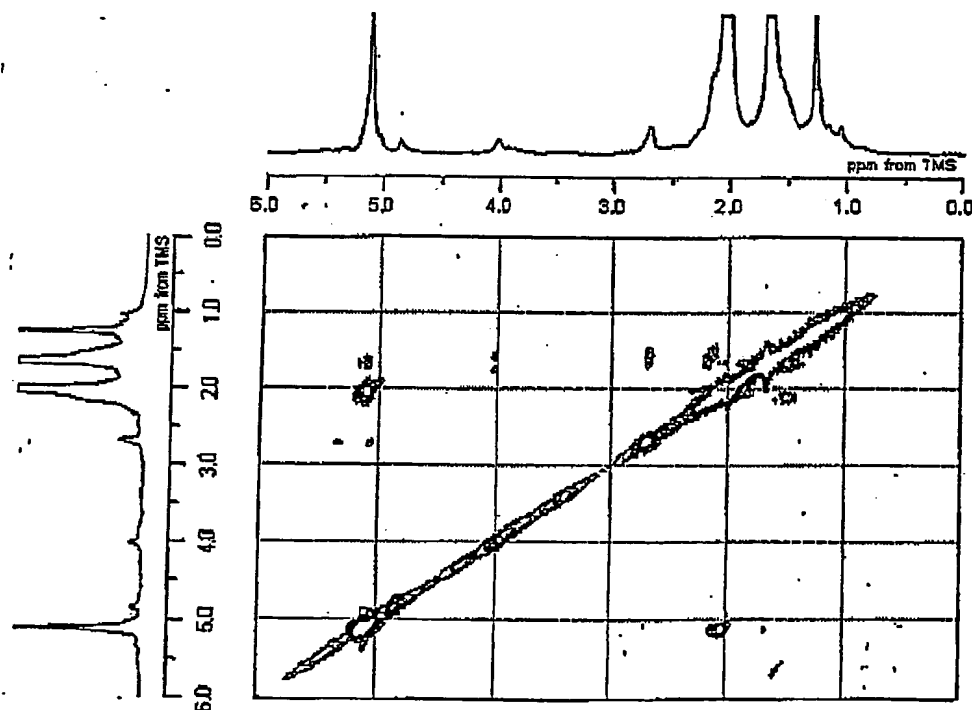


Figure 7. ^1H - ^1H correlation spectrum for carbonated DPNR.

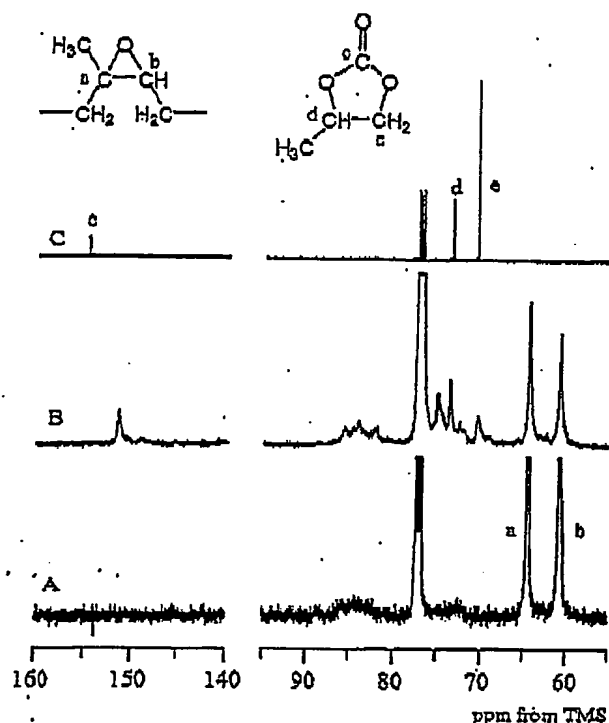


Figure 8. ^{13}C NMR spectra for (A) LEDPNR, (B) carbonated DPNR, and (C) propylene carbonate.

75 ppm of the methine group of the carbonate group is directly correlated to the ^1H signal at 4.0 ppm. The HMQC spectra are shown in Figure 10. In the HMQC spectra, the ^1H signal at 4.0 ppm is correlated to the ^{13}C signals at 28, 81, 83, 74, and 151 ppm. Because the signals at 28, 81, 83, 74, and 151 ppm have been assigned to primary (CH_3-), secondary ($-\text{CH}_2-$), secondary ($-\text{CH}_2-$), quaternary ($>\text{C}<$), and quaternary [$-\text{O}-\text{C}(\text{O})-\text{O}-$] carbons,¹⁵⁻¹⁷ it is proved that the ^{13}C signal at 75 ppm and the ^1H signal at 4.0 ppm can be assigned to the methine carbon and methine proton of the cyclic carbonate group, respectively, as shown in Figure 1.

Because the signal at 4.0 ppm was proved to be the methine protons of the carbonate group, the content of the carbonate groups (ξ) of the carbonated DPNR was estimated from the intensity ratio of the signals at 4.0 and 5.1 ppm:

$$\xi = \frac{I_{4.0}}{I_{5.1} / \{(100 - X_{\text{epoxy}}) / 100\}} \times 100 \quad (2)$$

The estimated ξ value is shown in Table 2. ξ was dependent on the conditions for the carbonation of LEDPNR. The most efficient carbonation occurred at 403 K and 20 MPa for 6 h. At a high temperature, that is, 423 K, a fragile product was prepared, perhaps because of an unexpected side reaction, whereas little carbonation proceeded at a low temperature. Thus, as long as we use LiBr as a catalyst without

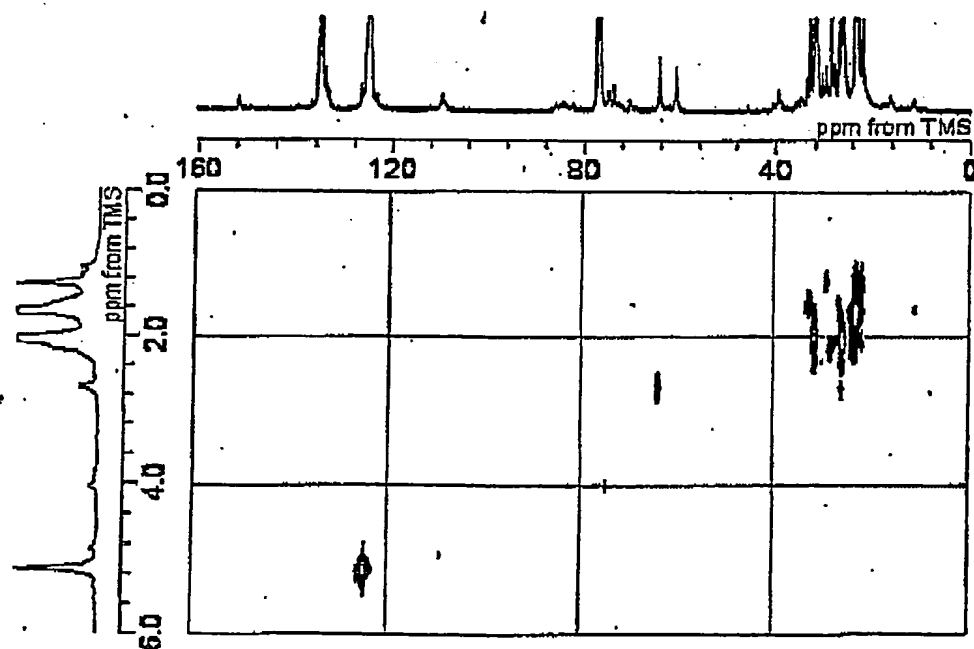


Figure 9. ^{13}C - ^1H correlation spectra for carbonated DPNR.

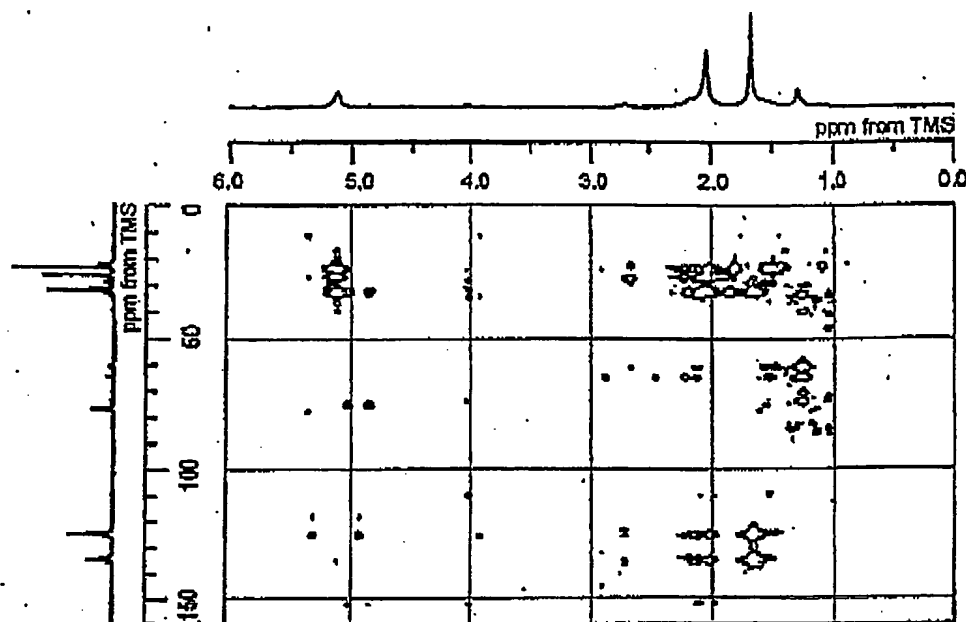


Figure 10. HMO spectra for carbonated DPNR.

any organic solvent, a suitable temperature and pressure for the carbonation of LEDP NR may be 403 K and 20 MPa, respectively.

In a subsequent article, we will report more detailed assignments and some properties of the carbonated DPNR.

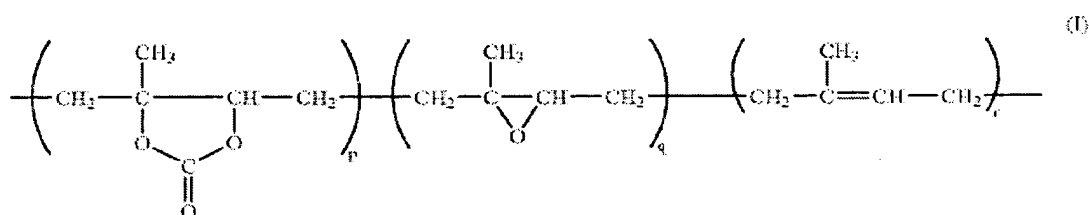
CONCLUSIONS

Carbonated natural rubber was prepared from LEDP NR and supercritical carbon dioxide with LiBr. After carbonation, new signals appeared at 4.0 ppm in the ^1H NMR spectrum and at 74, 75, and 151 ppm in the ^{13}C NMR spectrum, which were assigned to the methine proton, quaternary carbon ($>\text{C}<$), tertiary carbon ($>\text{CH}-$), and quaternary carbon [$-\text{O}-(\text{C}=\text{O})-\text{O}-$] of the carbonate group, respectively. ζ for the carbonated DPNR was estimated to be 7.2% at 403 K and 20 MPa.

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Although SU '262 does not disclose or suggest any cyclic carbonate-containing polymeric compound represented by formula (I),



as recited in claim 1, the Examiner asserted that because Example 2 of SU '262 discloses reacting epoxidized polyisoprene with carbon dioxide under the same reaction condition as disclosed in the present application, the reaction would result in the same compound as recited in claim 1. Office Action at page 3. The Examiner appears to consider the claimed compound to be inherently disclosed by SU '262, because the compound inherently would result from performance of the same reaction. Applicant respectfully disagrees for at least the following reasons.

To establish anticipation based on inherency, the extrinsic evidence "must make clear that the missing descriptive matter is necessarily present in the thing described in the reference, and that it would be so recognized by persons of ordinary skill." M.P.E.P. § 2112 (citing *In re Robertson*, 169 F.3d 743, 745 (Fed. Cir. 1999)(citation omitted)).

Although SU '262 discloses using polyisoprene as a starting material, SU '262 does not specify whether the polyisoprene is a synthetic polyisoprene or a natural rubber. It is well-known that synthetic polyisoprene inevitably contains considerable amounts of the products of 1,2- and 3,4- additions of isoprene monomers as repeating units in addition to the products of *cis*-1,4-additions of isoprene monomers. One of

ordinary skill in the art would know that it is impractical to synthesize polyisoprene containing 100 % of *cis*-1,4-polyisoprene. In contrast, natural rubber, corresponding to a starting material in the claimed invention, consists of the product of *cis*-1,4-additions, and does not contain products of 1,2- and 3,4-additions. In view of the above, the product produced by the method disclosed in Example 2 of SU '262, if a synthetic polyisoprene was used as a starting material, would inevitably have a different chemical structure from the structure represented by the above formula (I), as recited in claim 1.

Even if a natural rubber was used as a starting material in Example 2 of SU '262, the disclosed reaction would not produce the cyclic carbonated polymeric compound represented by the formula (I), as recited in claim 1, because, contrary to the Examiner's position, SU '262 does not perform the same reaction as disclosed in the present application, i.e., page 6, line 11- page 9, line 25, and as recited in the method claims. Specifically, SU '262 does not disclose that polyisoprene is deproteinized prior to an epoxidation step, as disclosed in the as-filed specification, e.g., page 8, lines 22-23, and as recited in amended claim 2.

Further support for the Applicant's position that deproteinization of natural rubber prior to the epoxidation step is necessary to produce the claimed cyclic carbonated polymeric compound is provided as follows, as disclosed in the references attached to this Reply, i.e., Kihara et al., J. Org. Chem. Vol. 58, pp. 6198-6202 (1998) ("Kihara"); Klinklai et al., Solid State Ionics, Vol. 168, pp. 131-136 (2004) ("Klinklai"); and Kawahara et al., J. Polym. Sci. Part A: Polym. Chem., Vol. 44, pp. 1561-1567 (2005) ("Kawahara").

Kihara discloses that cyclic carbonate formation reaction from an alkyl oxirane having epoxy group can proceed only when the epoxy group and a catalyst (a Li salt) forms an intermediate state (page 6201, Schemes III-V). When water is present in the reaction, even in a small amount, the catalyst will interact with water and fail to interact with epoxy group, as a result of which the cyclic carbonate formation reaction cannot proceed.

It is well known that natural rubber contains proteins and 0.5 to 3 % of water associated with the proteins. Klinklai discloses that it is impossible for epoxy groups contained in an epoxidized natural rubber to interact with a catalyst (a Li salt) unless the natural rubber has been deproteinized, since water associated with proteins interacts with the epoxy groups (page 132, col. 1, lines 1-6). Klinklai further discloses that when a deproteinized epoxidized natural rubber is employed, signal in a high-resolution solid-state ^{13}C NMR spectrum assigned to epoxy group is shifted, and also a glass transition temperature (T_g) in a DSC thermogram varies depending on the concentration of a catalyst (a Li salt) (Fig. 3; page 134, col. 1, lines 3-14), both of which reflect that the deproteinized epoxidized natural rubber can interact with the catalyst. Furthermore, Kawahara discloses that the cyclic carbonated natural rubber would not be produced when a natural rubber containing proteins is used as a starting material without being deproteinized (page 1561, col. 1, lines 20-26). One of ordinary skill in the art, with the above knowledge, therefore would conclude that a cyclic carbonated polymeric compound cannot be prepared unless natural rubber is deproteinized prior to an epoxidation step.

SU '262, in contrast, neither discloses nor suggests that natural rubber is deproteinized prior to an epoxidation step. In the Example 2 of SU '262, therefore, a halogenated tetra-alkylamine, a catalyst used in SU '262, would interact with water in proteins, preventing producing a cyclic carbonated polymeric compound as recited in claim 1, which implies that the Examiner's position that the reaction disclosed in Example 2 of SU '262 would necessarily result in the claimed compound is not accurate. The Examiner therefore has not established anticipation of claim 1, and its dependent claims, based on inherency. See M.P.E.P. § 2112.

Moreover, neither JP 573 nor Kawanami discloses, expressly or inherently, or suggests the claimed compound as recited in claim 1. Neither JP 573 nor Kawanami also discloses or suggests that natural rubber is deproteinized prior to an epoxidation step, missing from SU '262.

For at least the above reason, claim 1, and its dependent claims, are neither anticipated by, nor obvious over, SU '262, alone or in combination with JP '573 or Kawanami.

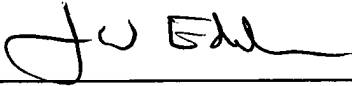
In view of the foregoing amendments and remarks, Applicant respectfully requests reconsideration of this application, withdrawal of the rejections, and timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: August 12, 2009

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Attachments:

- (1) Certified English translation of JP 2004-056275
- (2) Kihara et al., J. Org. Chem. vol. 58, pp. 6198-6202 (1998);
- (3) Klinklai et al., Solid State Ionics, vol. 168, pp. 131-136 (2004); and
- (4) Kawahara et al., J. Polym. Sci. Part A: Polym. Chem., vol. 44, pp. 1561-1567 (2005);